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(54) Title: FILM FOR PACKAGING FRESH FOOD

(57) Abstract

A packaging film consisting essentially of a terpolymer of ethylene, unsaturated monocarboxylic acid, an alkyl acrylate or methacrylate, and 0.1 to 2 weight percent of at least one sorbitan fatty acid ester, upon exposure to corona treatment exhibits good sealing properties and improved resistance to fogging.

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FILM FOR PACKAGING FRESH FOOD

BACKGROUND OF THE INVENTION

This invention relates to olefin-based polymer films suitable for packaging fresh meat, vegetables, and cheese.

Films used for packaging fresh meat, vegetables, and cheese must combine sanitary protection of the product, aesthetic appeal and handling characteristics suitable for use under a wide variety of conditions. The film must be strong, tough, glossy, and transparent. It must be resistant to the formation of water droplets on the inside surface of the film (referred to herein as "fogging") while in use. During the wrapping operation, the film is stretched, and it must conform to the shape of the material being packaged. The film must have sufficient "cling" to remain in place over the food product until heat sealing is effected, but it must also resist "blocking" so that unwinding from rolls is not impeded. It is also important that the film tear clearly and have high puncture resistance. Satisfactory sealing performance must be obtained under the wide variety of conditions encountered in commercial wrapping operations. Oxygen permeability must be sufficiently high that cuts of red meat maintain attractive color for three to four days.

Currently, fresh meat packaging films are usually highly plasticized polyvinyl chloride. There is a strong desire in the food industry to replace this material with non-halogenated, non-plasticized materials. Although many polyolefin-based compositions have been proposed, none have succeeded in meeting all the diverse needs of the market.

Japanese Application 53-134591-A discloses a packaging film whose components are (a) ethylene, (b) 9.7-2.0 mole % alkyl ester of an unsaturated carboxylic acid, (c) 0-2.5 mole % unsaturated carboxylic acid, and (d) 0.3-2.5 mole % metal salt of an unsaturated carboxylic acid. The film has good mechanical, thermal, and optical characteristics, including clouding resistance.

U.S. Patent 3,048,266 discloses fog resistant polyolefin films containing and anti-fog agent of ethylene oxide or polyoxyethylene esters or ethers, such as sorbitan mono-or di-esters of fat-forming fatty acids. Suitable film-forming polyolefins include polymers obtained from ethylene or propylene copolymerized with e.g. acrylic acids.

U.S. Patent 3,048,263 discloses fog resistant polyolefin films similar to those in U.S. Patent 3,048,266.

U.S. Patent 4,189,420 discloses a mixture of a polyolefin resin with a minor proportion of a polybutene of low molecular weight, a mixed glyceride, and preferably a surface wetting agent such as sorbitan fatty acid ester.

U.S. Patent 4,486,552 discloses fog-resistant polyolefin films of ethylene polymer, especially linear low density ethylene polymer, mixed with antifog agents such as (1) an alkoxylate alkyl phenol along with a mixed triglyceride, (2) a polyalkylene fatty acid ester, and (3) a combination of (2) and any part of (1).

U.S. Patent 3,541,040 discloses an antifogging polyolefin film produced from a mixture comprising polyolefin resin, sodium dioctyl sulfosuccinate, glycerol monostearate, and the reaction product of lauryl alcohol and ethylene oxide.

U.S. Patent 3,498,962 discloses olefin polymers containing sarcosine derivatives as antifog agents.

British Patent 1,206,089 discloses a composition comprising an olefin polymer such as polyethylene; 0.25 to 4% of the product of reaction between ethylene oxide and an alcohol of 8 to 18 carbon atoms; 0.1 to 2% of a polyhydric alcohol esterified with a fatty acid; and 0.05 to 0.75% of an alkali metal salt of a diester of sulphosuccinic acid and an alcohol. When made into a film, the composition allegedly does not suffer from fogging.

French Patent publication 2,117,386 discloses packaging film for fresh meat of ethylene vinyl acetate copolymer and 0.5-6% of an anti-blocking agent comprising a partial ester of a polyol and an aliphatic monocarboxylic acid or a polyalkyleneoxy derivative of the ester.

Japanese Application 53-108145-A discloses a resin composition comprising partially hydrolyzed vinyl acetate copolymer with minor amounts of low molecular weight polyolefin and sorbitan fatty acid ester. The resin is used to produce a stretch film with transparency, gloss, and fog resistance.

SUMMARY OF THE INVENTION

The present invention provides a packaging film comprising:

(a) at least 80% of a terpolymer of at least 50 weight percent ethylene, 2 to 20 weight percent of an unsaturated monocarboxylic acid having 3 to 8 carbon atoms, and 2 to 20 weight percent of a moiety derived from at least one alkyl acrylate, alkyl methacrylate, or mixtures thereof, where the alkyl radicals contain 2-12 carbon atoms, and further wherein the acid groups in the acid-containing moiety

are neutralized 0 to 10 percent by at least one metal ion; and

(b) 0.1 to 2 weight percent of at least one sorbitan fatty acid ester;

said film having been corona treated on at least one side to an extent sufficient to prevent fogging of the film when wrapped about a moist foodstuff.

The invention further provides a process for preparing a packaging film comprising the steps of:

(a) blending together a terpolymer of at least 50 weight percent ethylene, 2 to 20 weight percent of an unsaturated monocarboxylic acid having 3 to 8 carbon atoms, and 2 to 20 weight percent of a moiety derived from at least one alkyl acrylate, alkyl methacrylate, or mixtures thereof, where the alkyl radicals contain 1-12 carbon atoms, and further wherein the acid groups in the acid-containing moiety are neutralized 0 to 10 percent by at least one metal ion; and 0.1 to 2 weight percent of at least one sorbitan fatty acid ester;

(b) forming the blend into a film; and

(c) corona treating on at least one side of said film to an extent sufficient to prevent fogging of the film when wrapped about a moist foodstuff.

The invention further provides packages prepared by enclosing a foodstuff in such packaging films.

DETAILED DESCRIPTION OF THE INVENTION

The film of the present invention is primarily prepared from a terpolymer of ethylene which is prepared by the well-known free radical polymerization process, for example, at high temperature in a stirred, constant-environment reactor of the type described in U.S. Patent 4,351,931. The

chemical composition of the polymer is controlled by selection of appropriate monomer feed rates, as is well known.

The ethylene terpolymer comprises moieties derived from ethylene, about 2 to about 20 weight percent from an unsaturated monocarboxylic acid having 3 to 8 carbon atoms, and 2 to 20 weight percent from at least one alkyl acrylate, alkyl methacrylate, or mixtures thereof, where the alkyl radicals contain 1-12 carbon atoms. The monocarboxylic acids are preferably acrylic or methacrylic acid or mixtures thereof, and are preferably present in an amount of 4 to 12 weight percent, more preferably 5 to 10 weight percent, and most preferably 6 to 8 weight percent. The presence of the carboxylic acid moiety in the polymer provides the desired combination of clarity, strength, and puncture resistance.

Suitable alkyl acrylates or methacrylates are those having alkyl groups containing 2-12 carbon atoms, including propyl, isopropyl, n-butyl, isobutyl, n-pentyl, n-hexyl, n-octyl, 2-ethylhexyl, and n-dodecyl groups; methyl groups are not preferred. Isobutyl and n-butyl acrylate are most preferred. Such ester moieties are preferably present in an amount of 4 to 12 weight percent, more preferably 5 to 10 weight percent, and most preferably 6 to 8 weight percent. The presence of the alkyl acrylate or methacrylate in the polymer provides the desired high degree of stretchability and flexibility to the film.

The most preferred terpolymer comprises ethylene, methacrylic acid, and isobutyl acrylate, in view of its general acceptance for food-contact applications.

The polymer of the present invention can be used in the form of the unneutralized acid terpolymer,

or its acid groups can be neutralized with low levels of metal ions, e.g. up to about 10% neutralization. Suitable metals include those from groups I, II, III, IV-A and VII of the Periodic Table of Elements (as presented on page 392, Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., 37th ed.). In particular sodium, potassium, lithium, cesium, silver mercury, copper, berylium magnesium, calcium, strontium barium copper, cadmium, mercury, tin, lead, iron, cobalt, nickel, zinc, and aluminum may be suitable, although for food packaging applications those metals which are not particularly toxic are preferred. Zinc and sodium are most preferred.

It is generally preferred that the polymer be unneutralized, although a low level of neutralization can be desirable e.g. to improve such characteristics as melt stability. The amount of neutralizing metal ion, if any, should be sufficiently low so as to not unduly reduce the melt index of the resulting polymer. In order to form a suitable film it is desirable that the polymer have a melt index of 1 to 15, preferably 5 to 12, and most preferably 7 to 10 dg/min at 190°C, as determined by ASTM D-1238. At this preferred melt index, film of good quality can be produced at high rates at a melt temperature of about 180°C, thereby avoiding volatilization of the antifog additive.

The terpolymer may constitute the entire polymeric component of the film, although up to 18% or even 19.9% of other polymers may be added in amounts which to not negate the advantages of the present invention. In particular, small amounts of at least one second polymer such as an ethylene based homopolymer or copolymer may be added as a carrier resin, that is, providing a concentrate for addition

of a sorbitan fatty acid ester, described below. The amount of carrier resin will normally be 10% or less of the composition; levels of about 5% of a (binary) acid copolymer have been found to be quite suitable for this purpose. Normally the terpolymer will constitute at least 80%, preferably at least 90% by weight of the film.

To the polymer is added a low level of at least one sorbitan fatty acid ester. Sorbitan fatty acid esters are partial esters of sorbitol and its anhydrides with fatty acids, i.e., acids of 8 to 20 carbon atoms. The preferred ester is sorbitan monolaurate. The amount of the ester in the polymer is about 0.1 to about 2 weight percent, preferably 0.3 to 0.8 weight percent. The optimum concentration is about 0.5%. The presence of the sorbitan fatty acid ester provides improved antifog performance combined with freedom from blocking, while maintaining good film clarity.

The composition of the terpolymer and the sorbitan fatty acid ester is prepared by blending the two components together. Generally this blending will be performed in the melt phase. It is generally convenient to prepare a concentrate of the additive in a suitable olefin copolymer or terpolymer and then dry-blend pellets of the concentrate with terpolymer pellets before feeding to a film extruder. Other methods of incorporation can be used if desired, but in any event the addition of the sorbitan fatty acid ester will be effected before the terpolymer is melted and formed into a film.

The composition may be formed into a film, preferably by the well-known bubble extrusion and orientation process (i.e., the blown film process),

followed by collapsing, splitting, treating, and winding of the film.

Use of sorbitan ester in the terpolymer film does not of itself give satisfactory performance in terms of antifog performance, apparently because it does not migrate to the surface of the film to a sufficient extent to bring about the formation of a continuous water film, rather than discrete droplets. Application of corona treatment to one side of the film, however, enhances antifog and other desirable properties to an unexpected extent.

Devices suitable for corona treatment of films are well known in the art, and are described, for example, in U.S. Pat. 3,133,193. Generally, a suitable configuration includes a grounded metal roll with an insulated cover, and an electrode mounted parallel to the cylinder axis of the roll. The film passes over the insulated roll, and the corona is developed between the electrode and the film. The electrode gap, which is the distance between the electrode and the insulated roll cover, can be adjusted to obtain the desired level of wetting tension, as defined in ASTM D-2578, which is the measured control parameter. It is not possible to universally and specifically define all the suitable operating parameters for corona treatment, since these will depend on line speed, film width, configuration and cleanliness of the electrodes, additives present in the film, film temperature, and so on. However, it is well within the abilities of one skilled in the art to determine the wetting tension and to make appropriate adjustments in the pertinent parameters to obtain the desired level of wetting tension. A suitable range of treatment is that which provides a

wetting tension of 40 to 50 dynes/cm, preferably 42 to 48 dynes/cm.

The amount of energy applied to the film is important in that a certain minimum amount is needed in order to achieve the desired improvements in surface properties of the film. The corona treatment is preferably applied only to that side of the film which will be next to the package contents. Thus the blown film production line, corona treatment station, film splitters, and windup facilities should be assembled correctly to produce a final film roll which will feed into the food packaging machine with the desired orientation. It is, of course, possible to treat both sides of the film. The main effect of such double treatment is to adversely affect heat sealing performance, although under some circumstances a very light corona treatment on the second side may be useful. A variety of apparatus and geometrical arrangement are possible to achieve a suitable level of treatment, as will be apparent to one skilled in the art.

Example 1

Ninety-five parts by weight of a pelletized terpolymer of ethylene with 6 weight percent isobutyl acrylate and 6 weight percent methacrylic acid, melt index 9 dg/min (190°) was blended with 5 parts by weight of a pelleted concentrate of 10 parts sorbitan monolaurate in 90 parts ethylene methacrylic acid copolymer resin. The dry blend was extruded at 180°C melt temperature through a 50 mm single screw extruder equipped with a 100 mm diameter circular die to obtain 16 micrometer film. The film was prepared at a rate of 27 m/min in a blown film process in which the diameter of the blown bubble to that of the die was 4.5 to 1. The film thickness was 16 micrometers. One

surface of the film was corona treated using Kalwar™ corona equipment with the electrode gap and power settings adjusted to obtain a wetting tension on the film surface of 44 dynes/cm as measured by ASTM D 2578. The film was passed under the discharge at 27 m/min. The film obtained was transparent, glossy (gloss of 105% as determined by ASTM D 2454), and exhibited a high degree of cling and resilience as determined manually by stretching the film over the top of a wide-mouth jar, depressing it with a finger, and observing its recovery.

The film thus prepared was used to package fresh meat contained within a tray, using a Delford™ commercial meat-wrapping machine, manufactured by Delford Co. (Japan). This machine stretches the film, pushes the tray and contents through the web, brings the film down around the sides of the tray, and seals the film beneath the tray using a heat seal. The heat seal is formed in a front-to-back fashion between the inner and outer surfaces of the film. Rates of up to 50 packages per minute were achieved and the packages were attractive and smooth. A similar test was run on an Ilapak Targa™ Model 50A machine manufactured by Ilapak SA to package simulated food items. Performance in this machine was similarly very satisfactory.

Temperature settings of the heat sealing plate in the Delford™ machine were varied. It was observed that the film of the present invention could be sealed over a wide temperature range of 115 to 150°C while consistently obtaining fusion seals. Traditional olefin film for food wrappings have always exhibited undesirably narrow sealing ranges, typically only 5-10C° (110-120°C for ethylene/vinyl acetate copolymer). The sealing range for polyvinyl chloride

films is about 124-140°C, although PVC does not provide true fusion seals under these conditions, so leakage of liquid through such seals is common.

Examples 2-6

Additional films were prepared by the process of Example 1, except that the composition of the terpolymer was varied as indicated in Table I. In each case the extruded composition contained 0.5% sorbitan monolaurate and was corona treated on one side.

TABLE I

Ex.	Isobutyl Acrylate %	Methacrylic Acid %	Melt Index	Dart Drop[a]	Gloss[b] %	Haze[c] %
2	8	8	7	200	112	3.3
3	5	10	7	190	121	2.6
4	10	5	7	160	97	5.7
5	5	5	7	150	88	6.4
6	6	6	7	260	118	2.5

a. in g, according to ASTM D 1709.
b. ASTM D 2454.
c. ASTM D 1003.

All the films of Examples 1-6 passed a test for anti-fog performance. In this test film samples are stretched over the tops of two glass beakers half filled with water, and the beakers are placed either in a refrigerator at 8.8°C or in an oven at 35°C for up to 5 days. The beakers are observed frequently to see whether condensed water on the lower film surface forms droplets or a continuous film. If droplets form at any time, interfering with visibility, the film is deemed to have failed the test.

Examples 2, 3, and 6 were significantly superior to the others in optical properties and dart-drop puncture resistance.

Packaging tests were carried out as described for Example 1 using the films of Examples 2-5 on a "Mini" machine and W18 and W40 machines manufactured by Automac Industria SRL (Italy). The Mini is a semi-automatic machine, with hand feed and a hot plate sealer. The W18 and W40 are high speed automatic machines with heated conveyor sealing. With all of the films it was possible to abtain attractive, functional packages at rates typically used with these machines. The film of Example 3 was particularly superior in terms of tighness, clarity, and sparkle. Tests of the film of Example 6 on the Automac™ machine showed an excellent balance of performance characteristics, producing attractive packages at rates for which the packaging machine was designed.

Comparative Example A

Example 4 was repeated, but no corona treatment was applied. The film failed the fog test, since droplets appeared on the film after a few hours.

Comparative Example B

Example 4 was repeated, with corona treatment on both sides of the film to obtain wetting tension levels of about 45 dynes/cm. This film was unsatisfactory in heat sealing performance when tested over the range of 110 to 150°C.

Comparative Example C

Example 4 was repeated, with glycerol mono-oleate replacing the sorbitan monolaurate. This film failed the fog test.

Comparative Example D

Example 4 was repeated, with no antifog additive present, but with corona treatment applied to one side to obtain a wetting tension of 44 dynes/cm. The film performed very poorly in the fogging test, with droplets forming very rapidly.

Example 7

A film was prepared identical to that of Example 6 except that the terpolymer was neutralized with zinc ions to about a 5% level, thus reducing the melt index to about 5. The film was indistinguishable in performance from Example 6, passed the fog test, and was therefore rated as excellent.

The above examples show that polymer films of the present invention perform very well in packaging equipment designed for plasticized polyvinyl chloride film and can be used advantageously whenever non-halogenated package materials are required.

WHAT IS CLAIMED IS:

1. A packaging film comprising:

(a) at least 80% of a terpolymer of at least 50 weight percent ethylene, 2 to 20 weight percent of an unsaturated monocarboxylic acid having 3 to 8 carbon atoms, and 2 to 20 weight percent of a moiety derived from at least one alkyl acrylate, alkyl methacrylate, or mixtures thereof, where the alkyl radicals contain 2-12 carbon atoms, and further wherein the acid groups in the acid-containing moiety are neutralized 0 to 10 percent by at least one metal ion; and

(b) 0.1 to 2 weight percent of at least one sorbitan fatty acid ester;

said film having been corona treated on at least one side to an extent sufficient to provide a wetting tension of the treated surface of 40 to 50 dynes/cm.

2. The packaging film of claim 1 wherein the corona treatment has been applied to provide a wetting tension of 42 to 48 dynes/cm.

3. The packaging film of claim 1 wherein the terpolymer comprises moieties derived from ethylene, from methacrylic acid or acrylic acid, and from n-butyl acrylate or isobutyl acrylate.

4. The packaging film of claim 3 wherein the amount of methacrylic acid or acrylic acid moiety in the terpolymer is 4 to 12 weight percent and the amount of the n-butyl acrylate or isobutyl acrylate moiety in the terpolymer is 4 to 12 weight percent.

5. The packaging film of claim 4 wherein the amount of methacrylic acid or acrylic acid moiety in the terpolymer is 5 to 10 weight percent and the amount of the n-butyl acrylate or isobutyl acrylate moiety in the terpolymer is 5 to 10 weight percent.

6. The packaging film of claim 4 wherein the amount of methacrylic acid or acrylic acid moiety in the terpolymer is 6 to 8 weight percent and the amount of the n-butyl acrylate or isobutyl acrylate moiety in the terpolymer is 6 to 8 weight percent.

7. The packaging film of claim 1 wherein the acid moieties are unneutralized.

8. The packaging film of claim 1 wherein the acid moieties are 1-6% neutralized with sodium or zinc ions.

9. The packaging film of claim 3 wherein the melt index of the terpolymer is 4 to 12 dg/min at 190°C.

10. The packaging film of claim 1 wherein the sorbitan fatty acid ester is sorbitan monolaurate.

11. The packaging film of claim 10 wherein the amount of sorbitan monolaurate is 0.3 to 0.8 weight percent.

12. A process for preparing a packaging film comprising the steps of:

(a) blending together

(i) at least 80% of a terpolymer of at least 50 weight percent ethylene, 2 to 20 weight percent of an unsaturated monocarboxylic acid having 3 to 8 carbon atoms, and 2 to 20 weight percent of a moiety derived from at least one alkyl acrylate, alkyl methacrylate, or mixtures thereof, where the alkyl radicals contain 2-12 carbon atoms, and further wherein the acid groups in the acid-containing moiety are neutralized 0 to 10 percent by at least one metal ion; and

(ii) 0.1 to 2 weight percent of at least one sorbitan fatty acid ester;

(b) forming the blend into a film; and

(c) corona treating on at least one side of said film to an extent sufficient to provide a wetting tension of the treated surface of 40 to 50 dynes/cm.

13. The process of claim 12 wherein the corona treatment has been applied at a level of 42 to 48 dynes/cm.

14. The process of claim 12 wherein the terpolymer comprises moieties derived from ethylene, from methacrylic acid or acrylic acid in an amount of 4 to 12 weight percent, and from n-butyl acrylate or isobutyl acrylate in an amount of 4 to 12 weight percent.

15. The process of claim 12 wherein the sorbitan fatty acid ester is sorbitan monolaurate and comprises 0.3 to 0.8 weight percent of the blend.

16. A package comprising the film of claim 1 enclosing a moisture-containing food item.

17. A package comprising the film of claim 2 enclosing a moisture-containing food item.

18. A package comprising the film of claim 4 enclosing a moisture-containing food item.

19. A package comprising the film of claim 11 enclosing a moisture-containing food item.

20. The packaging film of claim 1 wherein the amount of terpolymer is 95%, the terpolymer comprises 88 weight percent ethylene units, 6 weight percent isobutyl acrylate units, and 6 weight percent methacrylic acid units, and has a melt index of 9 dg/min; the amount of the sorbitan fatty acid ester is 0.5%, and said ester is sorbitan monolaurate; and the film is corona treated on one side to provide a wetting tension of 44 dynes/cm; said film further comprising 4.5% of an ethylene/methacrylic acid copolymer resin.

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 90/00664

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[5]: C 08 J 5/18, C 08 L 23/08, C 08 K 5/10

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC[5]	C 08 J, C 08 L, C 08 K

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	WO, A, 84/03296 (THE DOW CHEMICAL) 30 August 1984 see abstract; page 6, lines 26-30; page 13, lines 18-23 cited in the application	1
A	FR, A, 2268049 (ASAHI-DOW) 14 November 1975 see claims 1,9	1
A	GB, A, 941757 (UNION CARBIDE) 13 November 1963 see page 2, lines 40-51,107-129	1

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* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
20th December 1990	
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	DWALCZYK

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	Patent Abstracts of Japan, vol. 3, no. 8, 25 January 1979, page 159M46, & JP, A, 53134591 (ASAHI DOW K.K.) 24 November 1978 see the abstract cited in the application --	1
A	DE, A, 2007219 (THE DOW CHEMICAL) 3 September 1970 see claim 1	1

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

EP 9000664
SA 36232

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 15/01/91
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